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ORIGINAL ARTICLE

Rhodium-catalyzed triarylphosphine synthesis via cross-coupling of aryl iodides and acylphosphines

Jiefang Yang [1], Hongyu Wu [1], Zhiqian Wang [*]

State Key Laboratory of Chemical Resource Engineering, College of Science, Beijing University of Chemical Technology, Beijing 100029, China

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KEYWORDS

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Abstract Rhodium(I)-catalyzed C–P cross-coupling reaction with aryl iodides and acylphosphines was disclosed for a straight forward synthesis of triarylphosphines. The acylphosphines were successfully employed as both the phosphorus source and the ligand to the Rh(I) catalyst. The triarylphosphines could be afforded in a yield up to 98% with good toleration of wide functional groups.

1. Introduction

Transition-metal-catalyzed carbon-heteroatom cross-coupling has become a fundamental strategy for functionalization of molecules [1]. The late transition metals, especially Pd, Ni, Cu, are mostly employed as the catalysts and realized various carbon-heteroatom (C–N, C–O, C–P etc.) coupling reactions [2]. Comparing to hetero atoms of the second row, the carbon-heteroatom coupling reactions with hetero atoms of the third row are more challenging for reasons such as the relatively low bond strength and the catalyst poisoning problems [1c,3c]. In recent years, the Rh(I) complexes scarcely employed before, are notably emerging as an efficient catalysts for C–X bond formation reactions, especially on the discovery of their good performances in challenging C–S and C–Si coupling reactions [3]. As to their neighbor atom, phosphorus, the C–P coupling reactions have been well realized by transition metal catalysts, such as Pd, Ni, Cu, and they are widely utilized in the syntheses of phosphine ligands [4]. Despite the hydrophosphorylation of unsaturated bonds [5], the C–P coupling reactions are much less developed and rarely reported with Rh(I) catalyst. To expand the catalytic activity of Rh(I) catalyst and develop the C–P bond coupling reactions, herein we report Rh(I)-catalyzed triarylphosphine syntheses via cross-coupling of aryl iodides and acylphosphines (Fig. 1).

2. Methods

2.1. General experimental methods

Unless otherwise noted, reaction temperatures are reported as the temperatures of the bath surrounding the vessel. Sensitive reagents and solvents were transferred under nitrogen in a glove-box using standard techniques. Proton nuclear magnetic resonance (^{1}H NMR) and carbon nuclear magnetic resonance

* Corresponding author.
[1] J. Yang and H. Wu contributed equally.
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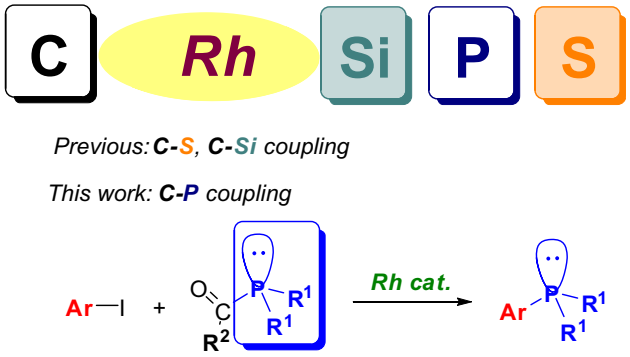


Figure 1 Rh-catalyzed C–X (3rd row) coupling.

(^{13}C NMR) spectra were acquired in $CDCl_3$ unless otherwise noted. Infrared (IR) spectra were obtained with a FT-IR series spectrometer as thin films on sodium bromide plates. Flash chromatography was performed using glass columns and carried out on SiO_2 (silica gel 200–300 mesh).

2.2. General procedure for the preparation of acylphosphines

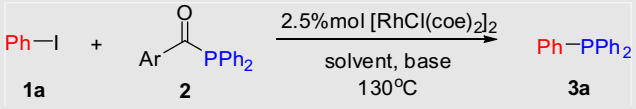
At 0 °C, under nitrogen, triethylamine (TEA) was added into a solution of diphenylphosphine in 10 mL Et_2O, followed by dropwise addition of benzoyl chloride. The mixture was stirred at 0 °C for 20 min, and then allowed to warm up to room temperature and stirred for another 6 h. The mixture was quenched with H_2O (10 mL) and the mixture was extracted with CH_2Cl_2 (2 × 50 mL). The combined organic phase was washed with brine (20 mL), dried over Na_2SO_4, and evaporated to give the crude product as yellow oil. The crude product was recrystallized from MeOH to afford pure product.

Diphenyl benzoylphosphine: According to the general procedure A, reaction with diphenylphosphine (0.98 g, 5.25 mmol), triethylamine (0.64 g, 6.3 mmol) and benzoyl chloride (0.77 g, 5.5 mmol) afforded 1.17 g of product in a yield of 77% as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ:7.98–7.96 (m, 1 H), 7.47–7.32 (m, 13H); ^{31}P (162 MHz, $CDCl_3$) δ:13.50; HRMS (ESI-QTOF) m/z: ($[M+H]^+$) Calcd. for $C_{19}H_{15}OP$: 291.0933 Found 291.0933; IR(film): 1643, 1433, 1201, 1180, 1141,1075, 740, 692 cm^{-1}.

2.3. General procedure for the preparation of triarylphosphines

In a sealed vial, under nitrogen, diphenyl-*p*-methoxylbenzoylphosphine (96 mg, 0.30 mmol, 1.5 equiv), $[RhCl(coe)_2]_2$ (3.6 mg, 5 mol% of Rh), aryl iodides (0.2 mmol), CsOPiv (93 mg, 0.4 mmol) and dioxane (0.4 mL) were mixed and stirred at 130 °C for 12 h. After the reaction completed, 2 mL H_2O was added, the mixture was extracted with ethyl acetate (3 × 5 mL). The combined organic phase was washed with brine and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the organic phase was concentrated, and the residue was purified by flash chromatography

Table 1 Cross-coupling reaction of iodobenzene **1a** with acylphosphine **2**.[a]



Entry	Ar	Solvent	Base	Yield (%)[b]
1	$HPPh_2$	Dioxane	CsOPiv	40[c]
2	4-MeOPh	Dioxane	CsOPiv	89(86[d])
3	4-MeOPh	Dioxane	–	< 5
4	4-MeOPh	Dioxane	CsOPiv	< 5[e]
5	4-MeOPh	Dioxane	CsOAc	77
6	4-MeOPh	Dioxane	Cs_2CO_3	54
7	4-MeOPh	Dioxane	*t*-BuOK	36
8	4-MeOPh	Dioxane	DABCO	56
9	4-MeOPh	Toluene	CsOPiv	< 5
10	4-MeOPh	DMF	CsOPiv	28
11	4-MeOPh	*N*-Me-morpholine	CsOPiv	83
12	4-MeOPh	Dioxane (0.5 eq H_2O)	CsOPiv	38
13	4-MePh	Dioxane	CsOPiv	62
14	Ph	Dioxane	CsOPiv	53
15	4-Cl Ph	Dioxane	CsOPiv	19
16	1-Np	Dioxane	CsOPiv	62

[a] Reaction conditions unless otherwise noted: iodobenzene **1a** (0.2 mmol, 1.0 equiv), acylphosphine **2**(0.3 mmol, 1.5 equiv), solvent (0.4 mL), base (0.4 mmol, 2.0 equiv), 2.5 mol% of $[RhCl(coe)_2]_2$, at 130 °C.
[b] ^{31}P NMR yield.
[c] $HPPh_2$ was employed instead of acylphosphine.
[d] Isolated yield.
[e] No catalyst was employed.

through silica-gel eluted with petroleum ether to give the desired product.

2.3.1. Triphenylphosphine (3a)

According to the general procedure B, reaction with diphenyl *p*-methoxylbenzoylphosphine (96 mg, 0.30 mmol, 1.5 equiv), $[RhCl(coe)_2]_2$ (3.6 mg, 5 mol% of Rh), iodobenzene (0.2 mmol), CsOPiv (93 mg, 0.4 mmol) and dioxane (0.4 mL) afforded 45 mg of product **3a** in a yield of 86% as a white solid; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.34–7.25 (m, 15 H). ^{31}P NMR (162 MHz, $CDCl_3$) δ: −5.36. MS (ESI) m/z: ($[M+H]^+$) Calcd for $C_{18}H_{16}P$: 263, Found 263. IR (film): 3067, 1474, 1431, 1087, 741, 694, 510,494 cm^{-1}.

2.3.2. [1,1′-biphenyl]-4-yldiphenylphosphine (3g)

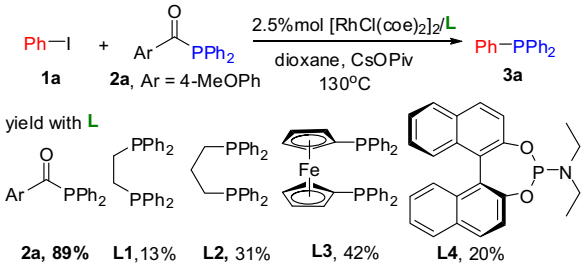
According to the general procedure B, reaction with diphenyl *p*-methoxylbenzoylphosphine (96 mg, 0.30 mmol), $[RhCl(coe)_2]_2$ (3.6 mg, 5 mol% of Rh), 4-phenyliodobenzene (0.2 mmol), CsOPiv (93 mg, 0.4 mmol) and dioxane (0.4 mL) afforded 48 mg of product **3g** in a yield of 70% as a white solid; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.58 (t, J = 8.0 Hz, 4 H), 7.50–7.32 (m, 15 H). ^{31}P NMR (162 MHz, $CDCl_3$) δ: −6.05.MS (ESI) m/z: ($[M+H]^+$) Calcd. for $C_{24}H_{20}P$: 339.13, Found 339.44. IR (film): 3052, 1479, 1433, 832, 761, 743, 695, 502 cm^{-1}.

2.3.3. 4-(diphenylphosphino)benzonitrile (3o)

According to the general procedure B, reaction with diphenyl *p*-methoxylbenzoylphosphine(96 mg, 0.30 mmol), $[RhCl(coe)_2]_2$ (3.6 mg, 5 mol% of Rh), 4-iodobenzonitrile (0.2 mmol), CsOPiv (93 mg, 0.4 mmol) and dioxane (0.4 mL) afforded 58 mg of product **3o** in a yield of 98% as a white solid; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.57 (d, J = 8 Hz,2 H), 7.39–7.31 (m,12 H). ^{31}P NMR (162 MHz, $CDCl_3$) δ: −4.27.MS (ESI) m/z: ($[M+H]^+$) Calcd. for $C_{19}H_{15}NP$: 288.09, Found 288.33. IR (film): 3048, 2221, 1488, 1433, 822, 693, 745, 549 cm^{-1}.

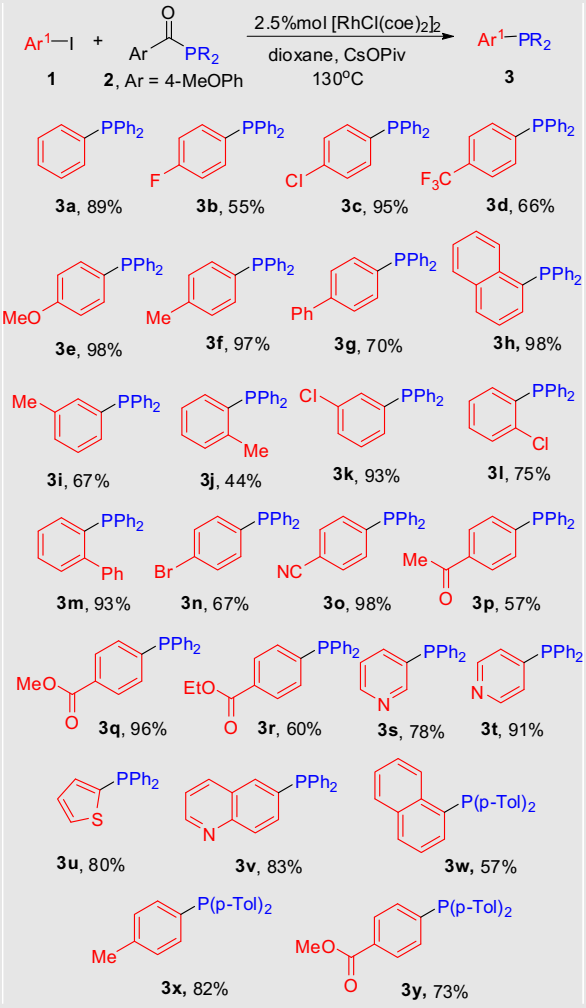
3. Results and discussion

The acylphosphines, prepared as key intermediates for the synthesis of polymerization photoinitiators [6], have been employed as electron-deficient phosphine ligands [7], and their character as phosphorus source was disclosed very recently [8]. The coupling reaction between iodobenzen **1a** and acylphosphine **2a** (Ar = 4-$MeOC_6H_5$) with $[RhCl(coe)_2]_2$ as the catalyst and cesium pivalate (CsOPiv) at 130 °C could afford product triphenylphosphine **3** in a yield of 89% (Table 1).



Scheme 1 C–P coupling reaction with various ligands.

Table 2 Rh-catalyzed C–P coupling with iodides **1** and acylphosphines **2**.[a]



[a] Reaction conditions: iodobenzene **1a** (0.2 mmol, 1.0 equiv), acylphosphine **2a** (0.3 mmol, 1.5 equiv), dioxane (0.4 mL), CsOPiv (0.4 mmol, 2.0 equiv), 2.5 mol% of $[RhCl(coe)_2]_2$, at 130 °C, isolated yield.

Under the same condition, the commonly used phosphorus source [9], secondary phosphine ($HPPh_2$), afforded product triphenylphosphine only in a moderate yield (entry 1, 2). The efficiency of this coupling reaction was greatly influenced by the addition of either organic or inorganic bases (entry 3, 5–8), though the mechanism is not well understood. Among the bases screened, the cesium salts [10], especially cesium pivalate (CsOPiv), was found to be more effective than other bases probably for their better solubility in dioxane. The solvent of this C–P coupling reaction influenced the yield greatly. The reaction in dioxane gave a much higher yield than in other nonpolar or strong polar solvents (entry 9, 10). It was still interesting to find a high yield (83%, entry 11) could be achieved in *N*-methylmorpholine, which is structurally similar to dioxane. The addition of water was harmful to achieve a high yield, even 0.5 equivalent of H_2O in reaction could draw the yield down from 89% to 38%, which is coincidently a same level as afforded by $HPPh_2$ (entry 12). The affection of acyl groups on the reactivities of acylphosphines was examined

by switching the substitution on the benzoyl group (entry 13–16). The electron donating group on the *para*-position showed a better reactivity than the electron withdrawing group, from methoxy to chloro group, the yields varied from 89% to 19%.

The ligands of metal center usually affect the reactivity of catalyst significantly,[10,11] various phosphine ligands were introduced to improve the yield of this coupling reaction based on previously optimized condition (Scheme 1). With the addition of bidentate phosphine ligands, such as dppe, dppp and dppf, or monodentate phosphoramidite ligand (**L4**), the yield decreased greatly to below 50% in all cases. These results indicated, besides as the phosphorus source, the acylphosphines could play as efficient ligands to the rhodium center to facilitate this coupling reaction.

The optimal parameters obtained were applied to the rhodium-catalyzed C–P bond formation with acylphosphines and a variety of aryl iodides (Table 2). With the *para*-substituted iodobenzene, the desired products could be afforded in yields arrange from 55% to 97%, and a trend of favoring electron-rich aryl iodides was observed (**3a**, **3e**, **3f** *vs*. **3b**, **3d**). As to the *ortho*- or *meta*-substituted iodobenzene, though the yield would decrease respectively, it still could reach as high as 98% with *ortho*-phenyl iodobenzene and 1-iodonaphthalene as the substrates. Some of potentially reactive functional groups in transition-metal-catalyzed reaction could be well tolerated in this reaction, especially the good selectivity between aryl bromide and iodide was observed. To our delight, the stronger coordinative heterocycles were well tolerated and successfully coupled with the diphenylphosphyl group in good to excellent yields (**3s-3v**), for example, 91% yield for 4-iodopyridine and 80% yield for 2-iodothiophene. Similar to the diphenylacylphosphine **2a**, di(p-)toyl acylphosphine **2e** could also be employed to generate triarylphosphines **3w**, **3x** and **3y** in yields from 57% to 82%. At present, this condition system appeared to be limited to aryl iodides coupling substrates, attempts with aryl bromides or triflates resulted in a yield less than 10% (determined by ^{31}P NMR, not shown), even under a higher temperature or longer reacting time.

4. Conclusions

In conclusion we have developed a Rh(I)-catalyzed C–P cross-coupling reaction with aryl iodides and acylphosphines for a straight forward synthesis of triarylphosphines. With cesium pivalate as the additive, the triarylphosphines could be afforded in a yield from 44% to 98% depending on the variation of substrate structure. In this reaction, the acylphosphines were employed successfully as both the phosphorus source and the ligands to the Rh(I) catalyst. To the best of our knowledge, this is the first C–P cross-coupling reaction between aryl iodides and phosphorylation reagents catalyzed by Rh(I) complexes.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jscs.2016.07.002.

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